



TITLE:

# The 7th Japan-Taiwan joint meeting on neutron and X-ray scattering

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**The 7<sup>th</sup> Japan-Taiwan joint meeting  
on neutron and X-ray scattering**

**Proceedings**

**March 11th ~ 12th, 2016**

**Edited by the organizing committee of The 7th Japan-Taiwan Joint meeting  
on neutron and X-ray scattering**

**Research Reactor Institute, Kyoto University**

## Preface

It is my honour to hold The 7<sup>th</sup> Japan-Taiwan joint meeting on neutron and X-ray scattering in Kumatori. The Japan-Taiwan joint meeting on neutron and X-ray scattering has been held bilaterally in Japan and Taiwan. In these meetings, we discuss the synchrotron X-ray and neutron scattering studies on bio-materials, soft-materials and nano-materials, and in addition we also discussed collaboration between Taiwan and Japan based on the synchrotron X-ray facility in Hsinchu, Taiwan and the neutron scattering facilities as well as the synchrotron facilities in Japan. The progress of this meeting is briefly followed. The 1<sup>st</sup> meeting was held at Tokai, Japan in December, 2006, the 2<sup>nd</sup> meeting was held at Wulai, Taiwan in December, 2007, the 3<sup>rd</sup> meeting was held at Kyoto, Japan in December, 2008, the 4<sup>th</sup> meeting was held at Yilan, Taiwan in March, 2010, the 5<sup>th</sup> meeting held at Tokai, Japan in February, 2013, the 6<sup>th</sup> meeting was held at Taipei, Taiwan in March, 2014, and the 7<sup>th</sup> this meeting is held at Kumatori, Japan in March, 2016.

This meeting will provide the recent outstanding results in the fields of fundamental polymer and biological sciences and their applications as well. In the fields of the X-ray and/or neutron scattering, the methodological progress expands the research fields and gives us new scientific insights. This meeting invites the researchers developing new methodologies, such as dynamics measurement utilizing nuclear Bragg resonance, subunit-kinetics measurement with deuteration-assisted small-angle neutron scattering and so on. I am anticipating that the participants find new methods to apply their research issues. In addition, neutron can be used not only for a probe to investigate a material structure but also for the medical purpose. A special lecture of the recent achievement and future perspective of Boron Neutron Capture Therapy will be provided by Prof. Ono, who is a pioneer of this therapy.

I am expecting that the collaboration between Taiwan and Japan will be enhanced through the scientific discussion and also personal understanding in this meeting.

Sincerely,

Masaaki Sugiyama

Chairman, The 7<sup>th</sup> Japan-Taiwan joint meeting on neutron and X-ray scattering

# **PROGRAM**

## **March 11<sup>th</sup>**

9:00-9:25 Reception

9:25-9:35 Opening Remarks

**Yuji Kawabata**  
(Director of Research Reactor Institute, Kyoto University)

### **SESSION 1 Chair: Go Matsuba**

9:35-9:55

The change with dispersion of silica in SBR under one-axis elongation  
by using time resolved USAXS method

**Shotaro Nishitsuji** (Yamagata University)

9:55-10:20

Phase and crystallization behaviors of copolymer blends with  
hydrogen-bonding interaction

**Chieh-Tsung Lo** (National Cheng Kung University)

10:20-10:45

Layer-by-Layer Single Crystals from Self-assembly of  
Triple-Crystalline Block Copolymers

**Yeo-Wan Chiang** (National Sun Yat-Sen University)

### **SESSION 2 Chair: Chieh-Tsung Lo**

11:00-11:25

Formation Mechanism of the Mesoporous Silica SBA-15 Thin Sheet  
with Perpendicular Nanochannels

**Chung-Yuan Mou** (National Taiwan University)

11:25-11:50

Effect of Coherence on Small-Angle Scattering

**Yuya Shinohara** (University of Tokyo)

11:50-12:15

Dynamics of Glass-Formers Studied by  
Gamma-ray quasi-elastic scattering method

**Makina Saito** (Kyoto University)

### **SPECIAL LECTURE Chair: Masaaki Sugiyama**

13:30-14:15

Boron Neutron Capture Therapy (BNCT) including

every element of the achievements in radiation oncology  
since the discovery of X-ray

**Koji Ono** (Kyoto University)

**SESSION 3 *Chair: Hideki Seto***

14:15-14:40

X-ray reflectivity studies on the mixed thiol capped Au  
nanoparticle/lipid monolayers

**Tsang-Lang Lin** (National Tsing Hua University)

14:40-15:05

Solvated structure and phase behavior of thermo-responsive  
polymer in ionic liquid

**Mitsuhiro Shibayama** (University of Tokyo)

15:05-15:30

Biological Hydrogels Formed by Swollen Multilamellar Liposomes

**Shih-Huang Tung** (National Taiwan University)

**SESSION 4 *Chair: Rong-Ming Ho***

15:45-16:10

Structural characterization of  
poly(3,4-ethylenedioxy-2,5-thiophene):poly(styrene sulfonate)  
dispersions and corresponding spin-cast thin films via small-angle  
X-ray scattering

**An-Chung Su** (National Tsing Hua University)

16:10-16:35

Structural Transitions of BAX after the Apoptotic Activation

**Orion Shih** (National Synchrotron Radiation Research Center)

16:35-17:00

Surface Characterization of Poly(fluoroalkyl acrylates) by  
Surface X-ray Diffraction/Scattering and Neutron Reflectivity

**Atsushi Takabara** (Kyushu University)

17:00-17:20

***Group Photo***

## **March 12<sup>th</sup>**

### **SESSION 5 *Chair: Wei-Tsung Chuang***

**9:00-9:25**

**SAXS and SANS study on the structural change of  
human stratum corneum induced by the treatment of  
surfactant solution**

**Takuji Kume (Kao Corporation)**

**9:25-9:50**

**Small-angle neutron and X-ray scattering studies on metallocene  
EPDM**

**Kazuki Mita (Mitsui Chemicals, Inc.)**

**9:50-10:15**

**Electrochemical Reaction of Carbon Film with Electrolyte Solution as  
Studied by Time-slicing Neutron Reflectometry**

**Masashi Harada (Toyota Central R&D Labs., Inc.)**

### **SESSION 6 *Chair: Tsang-Lang Lin***

**10:30-10:55**

**Fabrication of Perpendicular Nanoporous TiO<sub>2</sub> Thin Films through  
Templated Synthesis of Dendron-Jacketed Block Copolymers**

**Wei-Tsung Chuang (National Synchrotron Radiation Research Center)**

**10:55-11:20**

**An Effect of Aggregation States in Nafion Thin Films  
on Transport Properties**

**Daisuke Kawaguchi (Kyushu University)**

**11:20-11:45**

**Competition between Entropy and Enthalpy in the Binding of Melittin  
with ULV Vesicles of Different Phosphate Lipid Chain Lengths**

**Chun-Jen Su (National Synchrotron Radiation Research Center)**

### **SESSION 7 *Chair: Mikihiro Takenaka***

**13:00-13:25**

**SAXS combined with crystallography for structural studies on  
macromolecular complexes and functional flexibility of protein**

**Shu-Ying Sherry Wang (National Cheng Kung University)**

13:25-13:50

Liquid phase networks of conjugated polymers and carbon allotropes

**Jrjeng Ruan** (National Cheng Kung University)

13:50-14:15

Probing UV-Irradiated and pyrolyzed block copolymer micelles on a solid by grazing incident X-ray

**Ya-Sen Sun** (National Central University)

**SESSION 8 Chair: U-ser Jeng**

14:30-14:55

Dynamic quaternary structure of alpha-crystallin

**Rintaro Inoue** (Kyoto University)

14:55-15:20

The correlation between the mechanics of a lipid membrane and its cellular functions

**Yi-Fan Chen** (National Central University)

15:20-15:45

Structural insights into molecular assembly in the proteasomal systems

**Tadashi Sato** (Nagoya City University)

**SESSION 9 Chair: Mistuhiro Shibayama**

16:00-16:25

Current status and results on J-PARC/MLF

**Hideki Seto** (KEK)

16:25-16:50

Nanostructured Networks in Chiral Block Copolymers

**Rong-Ming Ho** (National Tsing Hua University)

16:50-17:15

Hierarchical Structure of Polymer/Nanoparticle Hybrid

**Hsin-Lung Chen** (National Tsing Hua University)

17:15

***Closing Remarks***

# The change with dispersion of silica in SBR under one-axis elongation by using time resolved USAXS method

Shotaro Nishitsuji<sup>1</sup>, Sho Suzuki<sup>1</sup> and Mikihiro Takenaka<sup>2</sup>

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Recently, from the viewpoint of the environmental problems and the depletion of fossil fuel resources, the high performance of tire is required. To achieve more high performance, it is important to investigate the relationship between the dispersion of filler in the rubber/filler system and the improvement of the mechanical properties. In the previous studies, the hierarchical structures in the rubber/filler system have been investigated by using a combined ultra small scattering and small angle scattering method of neutrons and X-rays[1,2]. In this study, the change with the dispersion of silica in Styrene-Butadiene Rubber (SBR) with one-axis elongation by using time resolved ultra small X-ray scattering (USAXS) was investigated.

SBR/Silica systems where the silica contents are 10, 15, 20, 25 vol% is prepared. Added weight fraction of the coupling agent to all the samples is 8 wt% of silica weight. Time resolved USAXS experiment was conducted at BL19B2, SPring-8, JAPAN.

The scattering pattern at 25 % of silica content before elongation and after elongation at 200 % as shown in Figure 1. Before elongation, the scattering pattern is isotropic. However, after elongation, the scattering pattern is anisotropic and is enhanced along elongation axis. This indicates the inhomogeneity of the dispersion of silica is enhanced along the elongation direction by one-axis elongation. From the analysis by Unified Guinier/Power-law approach, several characteristic parameters are estimated quantitatively, such as the size of aggregation and agglomerate, mass-fractal dimension. We will discuss the detail analysis by this approach and the change with the dispersion of silica in SBR quantitatively.

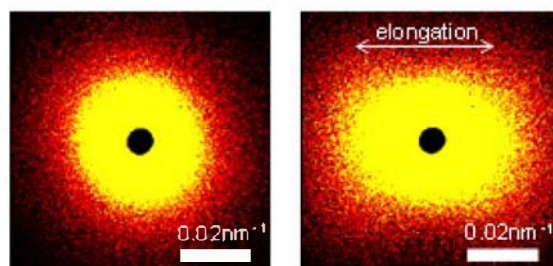


Fig.1 Scattering pattern at 25 % of silica content (a)before elongation and (b)after elongation at 200 %.

Acknowledgement : The samples in this study were provided from THE YOKOHAMA RUBBER CO., LTD.

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**Research Interests:**

- Polymer Physics
- Small Angle X-ray Scattering
- Polymer Blend

# Phase and crystallization behaviors of copolymer blends with hydrogen-bonding interaction

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We investigated the effect of the hydrogen-bonding interaction on the phase and crystallization behaviors of binary copolymer blends. In the blends composed of polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) and polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA) block copolymers, the hydrogen bonding between PEO and PAA improved the miscibility between the two molecules, which facilitated the localization of PS-*b*-PAA at the interface of the PS-*b*-PEO microdomains. However, the formation of hydrogen bonding decreased the crystallizable chain length of PEO, resulting in the occurrence of PEO crystallization within more confined region. As a result, the crystallization temperature of PEO decreased. By contrast, in the blends containing PS-*b*-PEO and polystyrene-*graft*-poly(acrylic acid) (PS-*g*-PAA) graft copolymer, PS-*g*-PAA was sequestered into the PEO domains, which caused swelling and increased the interfacial curvature that in turn, induced morphological transitions. Additionally, the hydrogen-bonded PEO and PAA in the PS-*b*-PEO/PS-*g*-PAA blends occurred in the middle or the free end of the PEO chains. The packing of PEO chains during crystallization was restricted by not only the chemically-linked PS-*b*-PEO interface but also the hydrogen-bonded PAA. This caused a substantial increase in the surface fold energy of PEO. As a result, a high degree of supercooling was needed to overcome the increased surface fold energy of PEO and crystallization occurred at a low temperature.

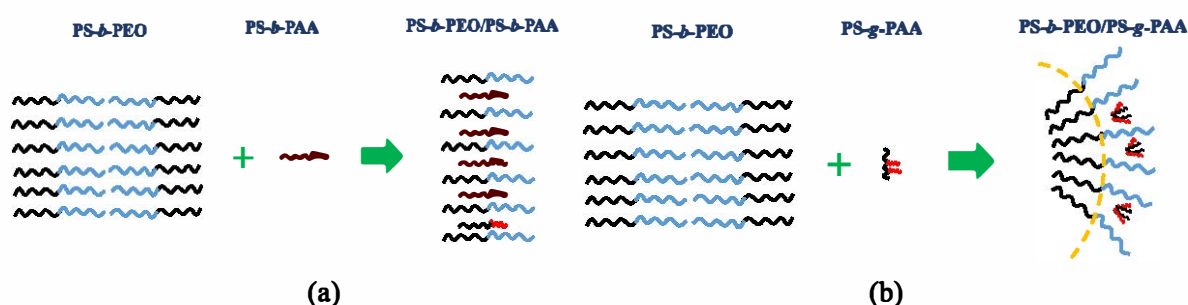


Figure 1. Schematic illustration of the phase behavior of blends with presence of hydrogen-bonding interaction. (a) PS-*b*-PEO/PS-*b*-PAA and (b) PS-*b*-PEO/PS-*g*-PAA.



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**Research Interests:**

- Polymer physics
- Polymer nanocomposites
- Polymer surfaces and interfaces

# Layer-by-Layer Single Crystals from Self-assembly of Triple-Crystalline Block Copolymers

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Manipulation of crystalline textures of biocompatible block copolymers is critical for the applications in the medical field. Here, we present the control of multiple-crystalline morphologies with flat-on chain orientation in biocompatible poly(ethylene oxide)-*block*-poly( $\epsilon$ -caprolactone)-*block*-poly(L-lactide) (PEO-PCL-PLLA) triblock copolymer thin films using melt and solvent-induced crystallization.<sup>[1]</sup> Only single-crystalline morphologies of the first-crystallized blocks can be obtained in the melt-crystallized thin films due to confinement effect. With solvent annealing by PCL-selective toluene, single-crystalline PLLA to double-crystalline PLLA/PCL and to triple-crystalline PLLA/PCL/PEO layered crystals in sequence are observed for the first time. With the control of solvent selectivity, different sequential crystallization involving first-crystallized PCL transferring to double-crystalline PCL/PLLA is obtained using PEO-selective *n*-hexanol for annealing. Surprisingly, the crystalline growth of the tri-layered single crystal exhibits specific layer-by-layer epitaxial relationship. As a result, the multiple-crystalline textures of the PEO-PCL-PLLA thin films can be carried out by controlling solvent and polymer interaction.

## References

[1] Y.-W. Chiang, \* S.-H. Huang, S.-W. Kuo, *Macromolecules*, 48, (2015) 8526.



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**Research Interests:**

- Self-assembly of Block Copolymers and Supramolecules
- Phase Behavior of Crystallizable Block Copolymers
- Block Copolymer Photonic Crystals

# Formation Mechanism of the Mesoporous Silica SBA-15 Thin Sheet with Perpendicular Nanochannels

Yi-Qi Yeh<sup>1</sup>, U-Ser Jeng<sup>1</sup> and Chung-Yuan Mou<sup>2</sup>

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Mesoporous silica SBA-15 thin sheets with perpendicular nanochannels, SBA( $\perp$ ), was synthesized by using the ternary surfactant system of SDS (sodium dodecylsulfate) – CTAB (hexyltrimethylammonium bromide) – P123 (PEO<sub>20</sub>-PPO<sub>70</sub>-PEO<sub>20</sub>).<sup>1-4</sup> The SBA( $\perp$ ) structural features, 2D hexagonally arrayed nanochannels, was considered deriving from the nonionic triblock copolymer P123. The SDS-CTAB system was proposed to function as a bilayer membrane to confine the co-organizing P123 and silicates. With neutron scattering, P123 displays strong scattering length density (SLD) contrast than deuterated SDS (d-SDS), deuterated CTAB (d-CTAB), and silicates in D<sub>2</sub>O solvent. In X-ray scattering, silicates exhibits strong SLD than the surfactants. In this report, we investigated the role of P123 micellization and the co-assembly process of silicate-surfactant system to realize the SBA( $\perp$ ) formation mechanism using both SANS and SAXS.

The charge condensation effect (varying(d-SDA)/P123,  $R_c$ : 0~128.75, in SDS-CTAB-P123 surfactant template) suggested a transformation of P123 micelles from sphere to prolate. An increase in aspect ratio of prolate micelles with increasing ionic surfactant (d-SDS)/(d-CTAB) concentration until  $R_c$  25.75. With excess ionic surfactant, the aspect ratio of the prolate would be reduced. The charge optimization effect (varying (d-SDS)/(d-CTAB)),  $R_o$ : 1.2 - 2.0, in SDS-CTAB-P123 surfactant template) showed all the micelles behaved as prolate micelle and the best recipe of  $R_o$ =1.5 exhibits the highest aspect ratio ~2.9.

The structural evolution during the co-assembly process of surfactant and silicates revealed three transitions as following: (1) The surfactant-silicate prolates would align and form lamellae phase between ionic surfactant bilayers in vesicle. (2) The surfactant-silicate prolates between two vesicles would polymerize due to hydrogen-binding of silicates. The fluctuation between the bilayer would supposedly reduce the lamellae ordering. (3) The elongated surfactant-silicate prolates would transform into well-aligned cylinders and form 2D hexagonal mesostructured. The TEM results also support the proposed surfactant template and co-assembly processes.

## References

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- [2] Y-Q. Yeh, H.P. Lin, *Langmuir* 2006, 22, 6
- [3] Y-Q. Yeh, C-Y. Tang, and C-Y. Mou, *J. Colloid Interface Sci.* 2011, 362, 354
- [4] Y-Q. Yeh, C-Y. Tang, and C-Y. Mou, *APL Mater.* 2014, 2, 113303



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**Research Interests:**

- Catalytic oxidation by gold nanoparticles
- Nanoporous nanomaterials as a drug/enzyme delivery carrier in Biomedicine
- Studies of supercooled confined water

# Effect of Coherence on Small-Angle Scattering

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Coherence is a fundamental concept for discussing scattering phenomena. Despite its importance, it is mostly ignored in the textbook of scattering of X-rays and neutron. Recent progress in X-ray brilliance makes it possible to conduct experiments utilizing coherence of X-rays: coherent diffraction imaging for the real-space visualization of materials' structure and X-ray photon correlation spectroscopy for monitoring the dynamics of nano-scale. In these techniques, the concept of coherence is explicitly utilized.

We have recently realized that the coherence may affect the scattering intensity profiles even when the incident X-ray is not fully coherent [1]. According to standard textbooks of small-angle scattering, scattering intensity profiles correspond to the fluctuation part of scattering length density, while a forward scattering at  $q = 0$  is not explicitly considered, where  $q$  is the magnitude of scattering vector. Recent advances in X-ray brilliance and X-ray optics make it possible to conduct scattering measurement at ultra-small angles with a small beam size. We have found that the measurement at such a low  $q$  leads to a significant contribution from the forward scattering on the measured scattering intensity profiles. The degree of contribution depends on the coherent length of incident X-rays, regardless of whether the beam is fully coherent or not. In this presentation, we will discuss the effect of coherence on small-angle scattering and perspectives on ultra-small-angle scattering.

## References

- [1] Y. Shinohara and Y. Amemiya, *J. Appl. Cryst.*, 48, (2015) 1660-1664.





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**Research Interests:**

- Development of X-ray scattering technique

# Dynamics of Glass-Formers Studied by Gamma-ray quasi-elastic scattering method

Makina Saito<sup>1</sup>, Makoto Seto<sup>1</sup>, Ryo Masuda<sup>1</sup>, Yasuhiro Kobayashi<sup>1</sup>, Shinji Kitao<sup>1</sup>,  
Masayuki Kurokuzu<sup>1</sup> and Yoshitaka Yoda<sup>2</sup>

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When liquids are cooled toward the glass transition temperature avoiding crystallization, the microscopic relaxation time or viscosity, in some cases, changes more than 10 orders of magnitude in a narrow temperature range without an apparent structural change. Understanding the mechanism is one of the most important aim of the glass transition study. A relaxation process known as the  $\alpha$  process, which is the structural relaxation process associated with the molecular diffusion, is directly related to the dynamical behaviour. With cooling the liquid, the other relaxation process emerges as its relaxation time branches from the relaxation time of the  $\alpha$  process. The process is called the slow  $\beta$  (Johari-Goldstein) process and its origin is still controversial. The branching process seems to be a key to understand the glass transition and the molecular dynamics in deeply supercooled liquids.

To examine the decoupling phenomenon from the microscopic point of view, a typical glass formers *o*-terphenyl [1] and polybutadiene have been studied [2] by the quasi-elastic scattering measurement known as a time-domain interferometry (TDI) method using gamma rays from <sup>57</sup>Fe nucleus excited by synchrotron radiation [3]. This method is a time-domain analogue of the conventional Rayleigh scattering Mössbauer radiation method [4]. Generally by a quasi-elastic scattering method, the relaxation time of microscopic structures with a certain microscopic length scale  $l \sim 2\pi/q$  can be selectively studied, where  $q$  is the momentum transfer of the gamma ray to the liquid sample decided by selecting the scattering angle of the detector. Owing to the atomic wavelength of the <sup>57</sup>Fe gamma-ray  $\sim 0.087$  nm (corresponding energy  $\sim 14.4$  keV) and its relatively narrow energy width  $\sim 4.7$  neV, the atomic and molecular dynamics can be studied in the time range of ns  $\sim$   $\mu$ s. We introduce a new result obtained by the TDI method on the glass formers.

## References

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- [4] D. C. Champeney and F. W. D. Woodhams, *J. Phys. B.*, 1, 1620 (1968) and references therein.



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**Research Interests:**

- Topic 1 Quasi-elastic scattering
- Topic 2 Glass transition phenomenon
- Topic 3 Soft matter

# **Boron Neutron Capture Therapy (BNCT) including every element of the achievements in radiation oncology since the discovery of X-ray**

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When the history of radiotherapy is traced, the achievements are summarized as below.

1. Focusing of the radiation dose on the tumor definitely increase the cure rate of tumor without increasing the incidence and grade of adverse effects. The success by brachytherapy, treatment by small radioactive source, is the solid evidence. This paradigm was also proved by IORT(intraoperative radiotherapy), stereotactic RT, conformal RT, IMRT(intensity modulated RT), charged heavy particle therapy et al.
2. Physiologically moving organs like as the tongue were also treated successfully by brachytherapy. To recreate this success in an external RT, the machine of which the X-ray beam can track the moving tumor in the target organ on respiration, was developed in Japan.
3. High LET radiation is very effective for the tumors which are refractory to X-rays. Carbon ion therapy was prove to successfully treat the soft tissue tumor or bone sarcomas which are radioresistant to X-rays. as the tumour cell selective cancer therapy

BNCT includes every element of these achievements. The idea of BNCT was proposed in 1932 based on the feature of  $^{10}\text{B}(n,\alpha)^7\text{Li}$  reaction. The cross section of this reaction is 2000 times larger than that of  $^{14}\text{N}(n,p)^{14}\text{C}$  reaction. Moreover the particles have extremely short ranges which are shorter than the diameter of general cells, hence, these particles destroy the tumour cells selectively if  $^{10}\text{B}$  accumulates in tumour cells selectively. The particles are also high LET radiation and then have large RBE (relative biological effectiveness). The first clinical study started in 1951 in US after the 2<sup>nd</sup> World War because the nuclear reactor was necessary as a neutron source. Unfortunately this trial failed to indicate the benefit of BNCT. The clinical research was succeeded by Japanese researchers since 1968. They used better  $^{10}\text{B}$ -compound, BSH, and achieved fairly nice result. It was 1987 when the clinical BNCT changed dramatically. BPA appeared as the clinically applicable 2<sup>nd</sup>  $^{10}\text{B}$ -compound this year. BPA actively accumulates in cancer cells, with that, BNCT has become cancer selective treatment in true meaning. Development of  $^{18}\text{F}$ -BPA PET(positron emission tomography), proposal of CBE(compound biological effectiveness) factor, success of BNCT for the recurrent H & N cancer, the world's first cyclotron based neutron source for clinical BNCT and start of the clinical test in 2012 were major progresses of BNCT since the appearance of BPA. Many of these achievements were developed by KURRI researchers and their colleagues. BNCT seems to be a completed form of radiotherapy.



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**Research Interests:**

- BNCT
- Radiation Oncology
- Radiation Biology

# **X-ray Reflectivity Studies on the Mixed Thiol Capped Au Nanoparticle/Lipid Monolayers**

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The Langmuir-Blodgett films of thiol capped gold nanoparticles mixed with zwitterionic lipid, dipalmitoylphosphatidylcholine (DPPC), were investigated by X-ray reflectivity, grazing-incident scattering, and transmission electron microscopy (TEM). The synthesized gold nanoparticles have an average diameter around 2 nm, and the gold nanoparticles were capped with 1-propanethiol, 1-octanethiol and 1-dodecanethiol, respectively. The monolayers were transferred onto silicon wafers for X-ray analysis and onto copper grid for TEM analysis. As revealed by X-ray reflectivity, for the mixed 1-octanethiol capped Au nanoparticle/DPPC monolayer system, at low compression pressure, the 1-octanethiol capped Au nanoparticles form a monolayer on top of disordered lipid monolayer. When the surface pressure is increased, the disordered lipid monolayer becomes ordered and the 1-octanethiol capped Au nanoparticle monolayer stays on top of it. It is favorable for the hydrophobic thiol capped Au nanoparticles to sit on the hydrophobic lipid tails instead of staying at the water surface. It seems that thiol capped Au nanoparticles have strong affinity to form large closely packed domains on smooth hydrophobic surface. Since the thiol capped Au nanoparticles would prefer to stay on top of the lipid monolayer to avoid contacting with water, it would be difficult to disperse the thiol capped Au nanoparticles into the lipid monolayer. We also investigated the morphology of these three thiol capped Au nanoparticle monolayers. At compression pressure of 20 mN/m, the 1-propanethiol capped Au nanoparticles tend to form multiply folded layers as revealed by TEM, while the 1-dodecanethiol capped Au nanoparticles form monolayers in grains with thread-like thiol-capped Au nanoparticle clusters forming the grain boundaries. It seems that the 1-dodecanethiol capped Au nanoparticle monolayer has better stability again compression as compared with the 1-propanethiol capped Au nanoparticle monolayer.



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**Research Interests:**

- Colloids and interfaces
- Nanomaterials and biomaterials
- Neutron and X-ray scattering

# Solvated Structure and Phase Behavior of Thermo-responsive Polymer in Ionic Liquid

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Ionic liquids (ILs) consist of only ion species, and thus, they have unique solvent property such as high ion conductivity, electrochemical stability, nonvolatility and nonflammability. In polymer science, the combination of polymer materials with ILs permits the fabrication of functional soft materials possessing the unique properties of ILs. Recently, stimuli-responsive polymers in ILs have been developed and received a great deals of attention.<sup>1</sup> For example, poly(benzyl methacrylate) (PBnMA) and its derivatives show lower critical solution temperature (LCST) – type phase separation in hydrophobic IL ([C<sub>2</sub>mIm]<sup>+</sup>)[TFSA<sup>-</sup>], and their phase-separating temperature ( $T_c$ ) can be drastically changed by slight chemical modification on the side chain.<sup>2</sup> We performed small-angle neutron scattering (SANS) study on one of the PBnMA derivatives, PPhEtMA (poly(2-phenylethyl methacrylate)) in ionic liquid.

SANS experiments were carried out for PPhEtMA in deuterated ionic liquid,  $d_8$ -[C<sub>2</sub>mIm]<sup>+</sup>[TFSA<sup>-</sup>] at High-Flux Isotope Reactor in Oak Ridge National Laboratory, USA.  $d_8$ -[C<sub>2</sub>mIm]<sup>+</sup>[TFSA<sup>-</sup>] was prepared by the procedure well established in our research group. Fig. 1 shows the SANS profiles obtained for PPhEtMA in  $d_8$ -[C<sub>2</sub>mIm]<sup>+</sup>[TFSA<sup>-</sup>] at various temperatures, 288 K – 310 K. As can be seen from the figure, steep upturn was observed when temperature exceeded  $T_c$  (~ 309 K in  $d_8$ -[C<sub>2</sub>mIm]<sup>+</sup>[TFSA<sup>-</sup>]), indicating the appearance of large aggregates in this region. We evaluated the second virial coefficient,  $A_2$  by Zimm plot. The obtained  $A_2$  decreased and changed its sign from positive to negative with increasing temperature. The result indicated that compatibility of PPhEtMA into  $d_8$ -[C<sub>2</sub>mIm]<sup>+</sup>[TFSA<sup>-</sup>] decrease gradually with increasing temperature.

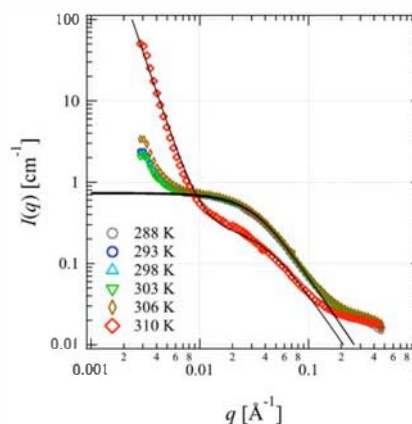


Figure. 1 SANS profiles observed for PPhEtMA /  $d_8$ -[C<sub>2</sub>mIm]<sup>+</sup>[TFSA<sup>-</sup>] solution at various temperature. The solid lines shows the fitting results by the Debye or Debye + Squared Lorentz functions.

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**Research Interests:**

- Structure characterization of hydrogels and ionic gels
- Structure of polymer micelles
- Molecular dynamics of thermosets

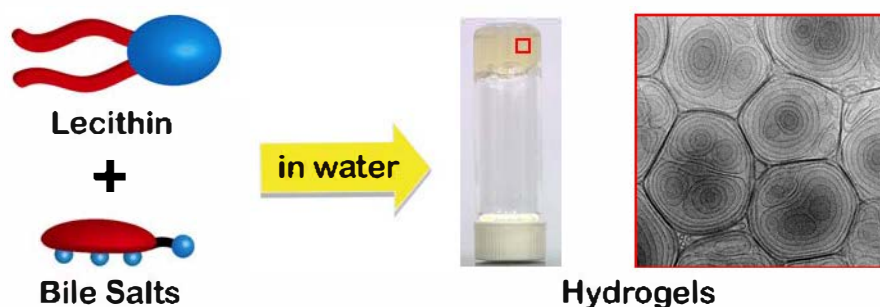
# Biological Hydrogels Formed by Swollen Multilamellar Liposomes

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The self-assembly of lecithin-bile salt mixtures in solutions has long been an important research topic, not only because they are both biosurfactants closely relevant to physiological functions but also for the potential biomedical applications. In this paper, we report an unusual biological hydrogel formed by mixing bile salts and lecithin at low bile salt/lecithin molar ratios ( $B_0$ ) in water. The gel can be prepared at a total lipid concentration as low as  $\sim 15$  wt% and the solid-like property of the solutions was confirmed by dynamic rheological measurements. We used cryo-TEM and SAXS/SANS techniques to probe the self-assembled structure and clearly evidence that the gel is made up of jammed swollen multilamellar vesicles (liposomes), instead of typical fibrous networks found in conventional gels. A mechanism based on the strong repulsion between bilayers due to the incorporation of negatively charged bile salts is proposed to explain the swelling of the liposomes. In addition to gel, a series of phases, including viscoelastic, gel-like, and low-viscosity fluids, can be created by increasing  $B_0$ . Such a variety of phase behaviors are caused by the transformation of bilayers into cylindrical and spheroidal micelles upon the change of the effective molecular geometry with  $B_0$ .



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- Self-assembly and phase behaviors of block copolymers
- Self-Assembly of amphiphilic biomolecules
- Rheology of complex fluids

# Structural characterization of poly(3,4-ethylenedioxy-2,5-thiophene):poly(styrene sulfonate) dispersions and corresponding spin-cast thin films via small-angle X-ray scattering

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Structural features of aqueous poly(3,4-ethylenedioxy-2,5-thiophene):poly(styrene sulfonate) (PEDOT:PSS) dispersions with the PSS-to-PEDOT mass ratio  $r = 2.5$  or  $6.0$  in the concentration range of  $0.2$ – $1.2$  wt% were characterized by means of small-angle X-ray scattering (SAXS). Results indicate that these dispersions generally comprise prolate nano-ellipsoids (with aspect ratio  $v \approx 5$ ) of aggregated PEDOT segments encircled by swollen coronae of anchored PSS chains. A major fraction ( $\phi_F \approx 0.9$ ) of these micelles are uniformly distributed in the aqueous matrix according to disordered packing of hard spheres. A minor fraction ( $\phi_F < 0.1$ ) of these micelles loosely inter-connect into domains of fractal dimension  $D_F \approx 1.9$ . There are also a minor fraction ( $\phi_O < 0.1$ ) of micelles with oblate core of  $v \approx 0.6$ , which corresponding to lateral agglomerates of the “normal” prolate cores. With increasing polymer concentration,  $\phi_F$  decreases whereas  $\phi_O$  increases, especially for the lower PSS content case of  $r = 2.5$ . This trend of agglomeration into oblate PEDOT cores with increasing polymer concentration extends into spin-cast films, where grazing-incidence small-angle X-ray scattering (GISAXS) profiles generally indicate interconnected prolate ellipsoids into fractal domains of  $D_F \approx 2.5$  but more significant presence ( $\phi_O \approx 0.2$ – $0.3$ ) of oblate PEDOT-rich domains, especially for the case of  $r = 2.5$ .



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- Structure-property relationship in polymeric systems
- Semiconducting polymers
- Nanomaterials

# Structural Transitions of BAX after the Apoptotic Activation

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In stressed cells, apoptosis ensues when BAX proteins oligomerize and permeabilize the mitochondrial outer membrane [1]. The mechanism utilized by BAX still remains elusive because BAX changes its functional structures along the apoptotic signaling pathway from cytosolic monomer, oligomer, to membrane-associated complex. This polymorphism of BAX poses a great challenge in tracing its structural transitions in functioning. Here we use a combination of electron spin resonance (ESR) and small angle X-ray scattering (SAXS) to study the conformational changes of BAX before and after the apoptotic activation. Particularly, an on-line HPLC is used to separate the BAX monomers, dimers, and oligomers in the eluted sample solution along the flow path for in-situ SAXS data collection at the 23A SWAXS endstation of National Synchrotron Radiation Research Center, Hsinchu, Taiwan [2].

The HPLC elution profile and previous ESR studies [3] indicate that there exist two forms of BAX monomer, UM and UM'. Upon the engagement of BimBH3, UM and UM' are transformed into a ligand-bound monomer (BM) and a oligomer (O), respectively. We construct the solution structures of BAX along the oligomerization pathway and show that BAX oligomers are assembled in solution via linear polymerization-like  $\alpha 6$  association. Our results specifically establish oligomerization interfaces and intermediates, which are important structural basis for manipulating BAX activity pharmacologically.

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**Research Interests:**

- SAXS from biological macromolecules
- NEXAFS of liquid microjets

# Surface Characterization of Poly(fluoroalkyl acrylates) by Surface X-ray Diffraction/Scattering and Neutron Reflectivity

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Polymers with fluoroalkyl ( $R_f$ ) groups are attractive to a broad range of applications in the paint and coatings sector. Surface properties of the fluoropolymers with perfluoroalkyl ( $R_f$ ) side groups depend on the surface molecular aggregation structure and surface molecular motion. Surface molecular aggregation structure and surface molecular motion of the poly(fluoroalkyl acrylate) (PFA- $C_y$ , where  $y$  is the fluoromethylene number of the  $R_f$  groups) and poly(fluoroalkyl methacrylate) (PFMA- $C_y$ ) were investigated by grazing incidence wide-angle X-ray diffraction (GI-WAXD) measurement, temperature dependence of the dynamic contact angle measurement, X-ray photoelectron spectroscopy (XPS) measurement in pseudo-hydrated state, and lateral force microscopy (LFM) measurement [1-3]. It was revealed that crystallization of FA side chain at the air interface contribute to the stable surface hydrophobicity of PFA- $C_y$  and PFMA- $C_y$ .

We utilized scattering length density contrast of fluoroalkyl group for neutron reflectivity(NR). The plasticization effects of compressed  $CO_2$  gas on the semicrystalline poly(FA- $C_8$ ) brush thin films (40 nm in thickness) grafted-from Si substrates were studied by NR[4]. *In situ* NR measurements were performed under the isothermal condition of  $T = 309$  K ( $\ll T_m$ ). The results showed the significant increase in the swelling of the polymer brush with increasing  $CO_2$  pressure. This indicates that the large sorption of  $CO_2$  molecules induces the melting of the semicrystalline poly(FA- $C_8$ ) brush at  $P > 4.1$  MPa.

This work was partially supported by the Photon and Quantum Basic Research Coordinated Development Program of MEXT, Japan

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**Research Interests:**

- Polymer Surface and Interfaces
- Nanocomposites
- Quantum Beam Analysis

# SAXS and SANS study on the structural change of human stratum corneum induced by the treatment of surfactant solutions

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The outermost layer of the skin, stratum corneum (SC) consists of corneocytes and intercellular lipid matrix, as shown schematically in Figure 1. The structure of the SC plays an important role in the barrier function [1, 2]. The surfactant used in skin cleansers sometimes induces swellings of SC. They are accompanied by structural changes of keratin fibers in the corneocytes, and the changes of intercellular lipids lamellar structure around the corneocytes. The aim of this research is to study the conformation change of human SC, particularly the soft keratin conformation, induced by the treatment of surfactant solutions using scattering analysis.

A problem emerged while conducting small-angle X-ray scattering (SAXS) measurements – the scattering of the surfactant micelles disturbed the observation of keratin fibers, particularly microfibril structures. To resolve this problem, the influence of the scattering of surfactant micelles was eliminated by using deuterated surfactant solutions in the small-angle neutron scattering (SANS) measurements, and observing only keratin fibers in the heel SC powder (without the intercellular lipids lamellar structures) was became possible [3]. Using this technique, we analyzed the swelling of the keratin fibers in SC powder soaked with the surfactant solution of various conditions.

On the other hand, since the SANS measurement required long time, several hours per one scan, it was difficult to pursue SC structural change in a short time (from several minutes to 1 hour) after surfactant solution soak. Therefore, the SC internal structure change was measured by SAXS for a short time using the structural orientation in the stacked SC sheets. And the SAXS measurement results after prolonged progress were compared with the SANS measurement results.

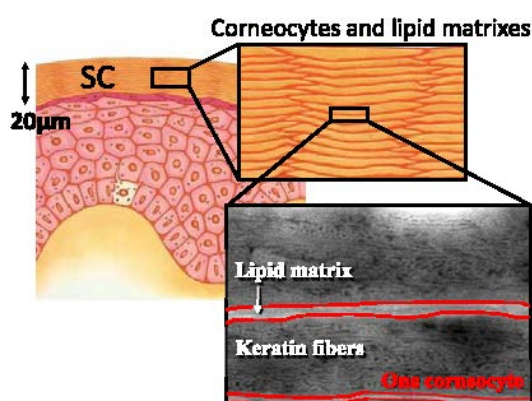


Figure 1. Schematic diagram of stratum corneum (SC) structure in the human skin

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**Research Interests:**

- Colloid and surface chemistry
- Soft matter
- SAXS and SANS

# **Small-angle neutron and X-ray scattering studies on metallocene EPDM**

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Linear ethylene-propylene-diene terpolymers (EPDM) and those having branch structures were obtained by metallocene catalysts, and network structures of the EPDMs crosslinked by peroxide initiated reactions were investigated by small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS). The neutron experiment at the BL20 Materials and Life Science Experimental Facility of J-PARC was performed under a user program (Proposal No. 2014AM0009). The synchrotron radiation experiments were performed at the BL03XU SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2013B7266, 2015A7216).



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**Research Interests:**

- Polymer physics
- Crystal and network structures
- Small-angle scattering

# Electrochemical Reaction of Carbon Film with Electrolyte Solution as Studied by Time-slicing Neutron Reflectometry

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Safety and durability of lithium ion batteries (LIBs) should be improved by understanding the nature of the solid-electrolyte interphase (SEI) that is formed at the boundary between the electrode and the electrolyte in LIBs. Thus, we have measured neutron reflectivity (NR) for an interface between a carbon film and a lithium-salt solution in a purpose-built half-cell under in-situ conditions.

The electrochemical reaction was conducted by linear sweep voltammetry from the open circuit voltage, 2.9 V, to 0.05 V against Li/Li<sup>+</sup>. When the potential fell below around 1.0 V at a rate of 0.2 mV/s, gradual change was observed for the spectra of NR. By fitting the time-sliced NR spectra with calculated curves using a series of scattering length density (SLD) profiles, time evolution of the profiles is demonstrated as shown in Figure 1. Beside a decrease in SLD of carbon layer, growth of a thin layer was found at the interface between the carbon and the solution, as the potential decreased down from 1.0 V. The SLD of the thin layer increased by 130 %, and the layer thickened from 20 to 42 nm. While the decrease in the SLD of the C film is attributed to the lithium insertion, the growth of thin layer could be assigned to the formation of the SEI. Although the composition of the SEI cannot be analysed only by NR experiments, we can estimate that the SEI should be the reaction products of the lithium electrolyte solution with less hydrogen and lithium atoms having negative scattering length.

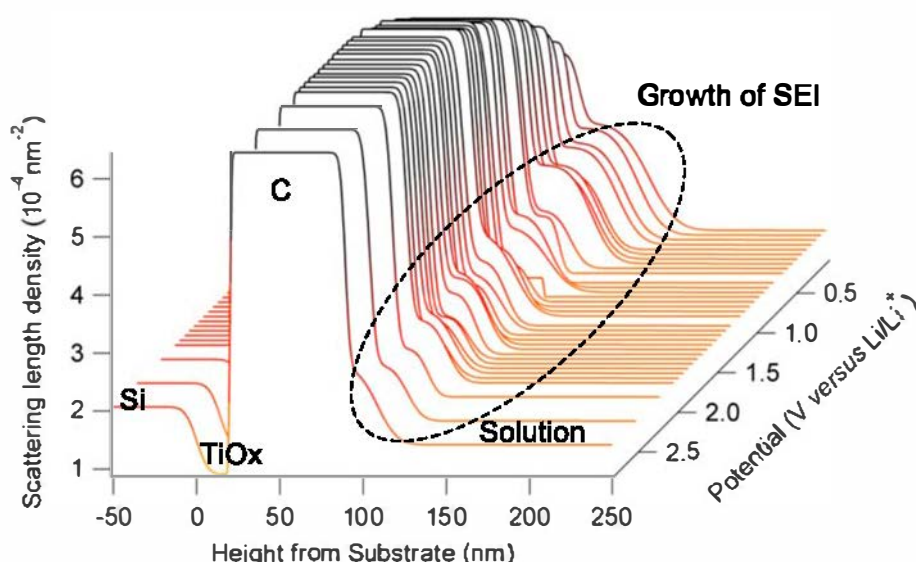


Figure 1 Evolution of the scattering length density profiles by decreasing the potential. Growth of SEI is observed at the interface of the carbon and the solution.



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**Research Interests:**

- Thin polymer film
- Colloidal dispersion
- Semi-crystalline polymer

# Fabrication of Perpendicular Nanoporous TiO<sub>2</sub> Thin Films through Templated Synthesis of Dendron-Jacketed Block Copolymers

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Direct template synthesis of highly density nanoporous conversion into TiO<sub>2</sub> (or metal oxides) is a challenge task for maintaining thermally robust and well-ordered framework. In this study we report a unique structural transformation process for perpendicular orientation of cylindrical microdomains in Dendron-Jacketed Block Copolymers (DJBCP)<sup>1-3</sup> and design a DJBCP-template synthesis for TiO<sub>2</sub> films consisting of high-density nanoporous anatase with perpendicular porosity. In order to understand the mechanism of the perpendicular orientation, we investigated time-resolved structural evolution of the doctor blade-cast films annealed at 150 °C using by GISAXS, AFM and TEM measured *ex situ*. The thin films of perpendicular cylinders can be fabricated into TiO<sub>2</sub> nanopores via a designed DJBCP-templated synthesis. This is a straightforward and cost-effective route to create large-area well-order 1D nanostructures for applications in optics, electronic, sensing, drug delivery, separation and nanolithography, because vertically aligned 1D nanostructures could potentially improve the charge-collection efficiency and effectively increase diffusion of guest species from outside.

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**Research Interests:**

- Structure and phase transitions in soft materials
- Polymer crystallization
- Block copolymer self-assembly

# An Effect of Aggregation States in Nafion Thin Films on Transport Properties

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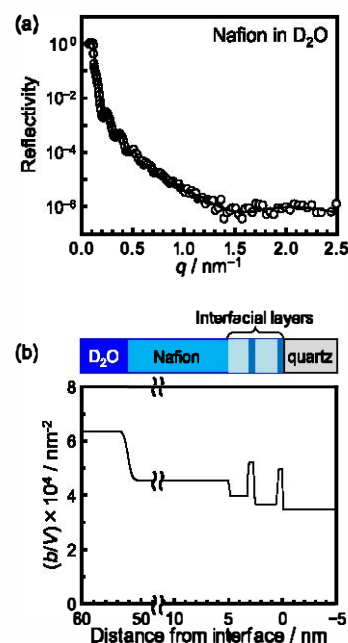
Nafion has been widely used as a proton exchange membrane in polymer electrolyte fuel cells (PEFC). Excellent electrochemical and mechanical properties of Nafion are associated with the characteristic network structure of the hydrated phase. Although downsizing PEFC is one of the interesting developments in the near future, it appears to us that most studies for Nafion conducted so far are limited to bulk systems. In this study, aggregation states, water sorption and proton conductivity in Nafion thin films prepared on quartz substrates were examined.

A Nafion thin film was prepared on a quartz substrate by spin-coating from Nafion dispersion in the water/alcohol mixture. The film was dried under vacuum at 313 K for 20 h and then immersed into D<sub>2</sub>O for 5 h to reach an equilibrium swollen state. A density profile of the film normal to the D<sub>2</sub>O interface was examined by neutron reflectivity (NR) measurement using Soft Interface Analyzer (SOFIA) at J-PARC.

Figure 1(a) shows a NR curve of the Nafion thin film in D<sub>2</sub>O. The solid line denotes the best-fit calculated reflectivity to the experimental one based on the model scattering density ( $b/V$ ) profile shown in Figure 1(b). The model containing interfacial multi-layers with a total thickness of ca. 5 nm gave a better fitting for the experimental data. The interfacial layers having lower and higher ( $b/V$ ) values than the internal region correspond to the hydrophobic and D<sub>2</sub>O-contained hydrophilic ones, respectively. This result clearly indicates that multi-layer structure was formed at the substrate interface. This may be due to the strong interaction between sulfonate groups in Nafion and quartz surface. The interfacial structure would affect the water sorption<sup>1)</sup> and proton conductivity in Nafion thin films. We will show results in the presentation.

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**Figure 1.** (a) Neutron reflectivity curve for a Nafion thin film on quartz substrate in D<sub>2</sub>O. Experimental data set is shown by symbol. The best-fit calculated curve using a model ( $b/V$ ) profile shown in (b) is



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**Research Interests:**

- Polymer thin films and interfaces
- Molecular motion of polymers

# Competition between entropy and enthalpy in the binding of melittin with ULV vesicles of different phosphate lipid chain lengths

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Concomitant polymer crystallization and nanoscale phase separation during spin-coating of polythiophene/fullerene films for polymer solar cells (PSCs) are traced using simultaneous grazing incidence small- and wide-angle X-ray scattering. The corresponding film thinning behavior observed using time-resolved UV–Vis reflectance reveals features of shear-flow-enhanced sol–gel transition and transient layering from vertical phase separation during the spin-coating process. The correlated results suggest that local phase separation, accelerated-nucleation-based polymer crystallization and fullerene aggregation, is initiated primarily within a surface layer developed during the sol–gel transition. Subsequently, the structural development is pinned, leaving only constant solvent dissipation through the surface layer until final film coarsening. The hence kinetically trapped network structure, featuring dispersed P3HT crystallites and PCBM nano-aggregates, guides the subsequent development over the optimized bulk-heterojunction structures of the spin-coated film. The shear-flow-enhanced surface layering process is a previously missing piece of information in our integrated understanding of the PSC film-formation process during spin-coating.

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**Research Interests:**

- Biopolymer self-assembled structure
- Polymer physics
- Small-angle x-ray scattering

# SAXS combined with crystallography for structural studies on macromolecular complexes and functional flexibility of protein

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The understanding of interactions between biological molecules is essential to comprehend the cellular processes in living organisms. Crystallography is a powerful tool to provide the interactive schemes of macromolecular complexes at atomic level. However, it is sometimes challenging and time consuming to crystallize large molecular machines. In this talk, I will present our work that combines crystallography and small-angle X-ray scattering (SAXS) to resolve the structures and functions of protein-DNA and protein-protein complexes. First, I will introduce our study on the peroxide response regulator PerR, a member of ferric uptake regulator (Fur) family, from *Streptococcus pyogenes*. We determined the crystal structure of PerR and resolved the first molecular architecture of PerR-DNA complex by SAXS analysis, revealing a unique DNA-binding topology distinct from currently proposed DNA-binding models for Fur family [1]. Second, I will introduce the work for studying the interactions between IL-1 cytokine members and their receptors. The activation of IL-1 signaling cascade, initiated by cytokine binding to ligand-recognition receptor and the following assembly of a co-receptor, triggers the subsequent intracellular signaling pathways. We conducted crystallographic and SAXS studies to understand how the functional flexibility of the IL-1 receptors contributes to specific interactions of cytokine-receptor complexes and how the intrinsic flexibility within IL-1 receptors relevant to molecular recognition [2].

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- Functional flexibility of macromolecules
- IL-1 signaling complex
- Zinc-finger DNA binding proteins

# Liquid phase networks of conjugated polymers and carbon allotropes

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Semiconductive conjugated polymers, including polyfluorenes and polythiophenes, normally are not miscible with insulating polymethylmethacrylate (PMMA) in molten state. Nevertheless, upon the dissolution effect of selected solvents, the liquid phase of PMMA was discovered to coexist with separate liquid phases of conjugated polymers. These polymer liquid phases are able to simultaneously distribute into networks or granular domains upon the variation of mixing ratios. Moreover, as being influenced by favourable  $\pi$ - $\pi$  interactions with conjugated polymers, functional materials like carbon nanotubes and fullerene derivatives were found to preferably blend into one of polymer liquid phases in these two-phase solutions, as shown in Figure 1. This is a new mechanism for establishing percolation network of functional carbon allotropes within polymeric thin film, providing opportunities of enhancing performances in various aspects, like heat and electronic conduction.

In addition to individual liquid phases of conjugated polymers, the network of phenyl-C61-butyric acid methyl ester (PCBM) liquid phase was found to develop in solutions also upon the addition of conjugated polymers. The involved phase separation can be adjusted by concentration, mixing ratio and the length of alkyl side chain attached on conjugated polymers as well. This prior phase separation is critical for later crystallization of PCBM within precipitated thin film, and networks of PCBM single crystal was found able to develop upon selected thermal treatment (Figure 2). According to these results, it is expected to establish a fundamental mechanism to manipulate the development of complex liquid phases in solutions as a novel way to reach desired structures of optoelectrical thin film.

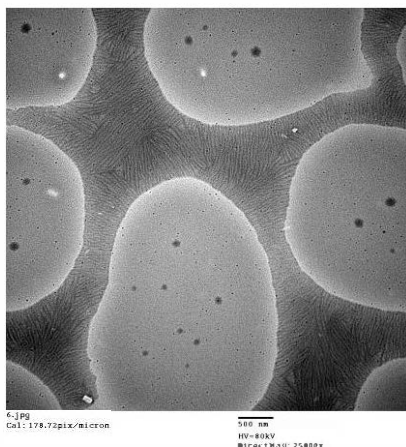


Figure 1. Electronic micrograph of preferable dispersion of carbon nanotubes within networks regions of polyfluorene of precipitated thin film

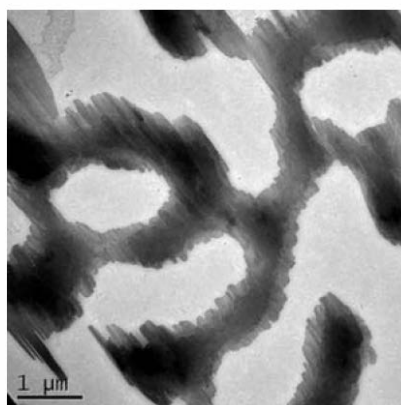


Figure 2. Electronic micrograph of networks of PCBM single crystals, which are covered with overgrowth of board-like crystallites





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- Ordering assembly and crystallization behaviors of organic molecules
- Polymer blends
- Phase transition behaviors

# Probing UV-Irradiated and pyrolyzed block copolymer micelles on a solid by grazing incident X-ray

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We investigated the structural evolution of truncated micelles in ultrathin films of polystyrene-*block*-poly(2-vinylpyridine), PS-*b*-P2VP, of monolayer thickness on bare silicon substrates (SiO<sub>2</sub>/Si) with UV irradiation in air- (UVIA) and nitrogen-rich (UVIN) environments. The structural evolution of micelles with UV irradiation was monitored with GISAXS measurements *in situ* while the surface morphology was probed with an atomic force microscope *ex situ* and the chemical composition with X-ray photoelectron spectra (XPS). This work provides clear evidence for an interpretation of relations between the structural evolution and photochemical reactions in PS-*b*-P2VP truncated micelles with UVIA and UVIN. Under UVIA treatment, photolysis and cross-linking reactions coexisted within the micelles; photolysis occurred mainly at the top of the micelles whereas cross-linking occurred preferentially at the bottom. The shape and size of UVIA-treated truncated micelles were controlled predominantly by oxidative photolysis reactions, which depended on the concentration gradient of free radicals and oxygen along the micelle height. Because of an interplay between photolysis and photo-crosslinking, the scattering length densities (SLD) of PS and P2VP remained constant. In contrast, UVIN treatments enhanced the contrast in SLD between the PS shell and P2VP core as cross-linking dominated over photolysis in the presence of nitrogen. The enhancement of the SLD contrast was due to the varied degree of cross-linking under UVIN for the PS and P2VP blocks.<sup>[1]</sup>

Next, we developed a method to fabricate arrays of nanostructured carbon materials of high quality, via direct pyrolysis of poly(styrene-*b*-2-vinylpyridine) (PS-*b*-P2VP) block copolymer (BCP) as thin films without small organic molecules incorporated as carbon resources. Prior to pyrolysis, the nanodomains were cross-linked with UV radiation under nitrogen (UVIN). As upon pyrolysis thermal energies impart mobility to nanodomains to overcome the constraints imposed by cross-linked chains, the free surface is inevitably covered with the PS block that has a smaller surface energy; unless favorable interactions with the P2VP block exist at the free surface, the outer layer of carbonaceous films is predominantly composed of the pyrolyzed PS block.<sup>[2-3]</sup>

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- Polymer thin films
- crystallization Behavior of Crystallizable Block Copolymers and Semicrystalline Homopolymers
- Self-assembly of soft matters

# Dynamic Quaternary Structure of $\alpha$ -Crystallin

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Most of proteins possess proper quaternary structures. Such quaternary structures are not necessarily fixed to certain configurations, but rather are fluctuating due to internal dynamics. Interestingly, some of the proteins possess unique quaternary structures and the representative examples of such proteins are small heat-shock proteins (sHSPs). A small monomer with molecular mass ranging from 9 to 43 kDa serves as a building component for assembling into larger oligomeric structures. Such oligomeric structures are strongly influenced by even the subtle change of external environment.

The  $\alpha$ -crystallin, which has the consensus amino acid sequence to sHSPs, is comprised of two subunits:  $\alpha$ A-crystallin and  $\alpha$ B-crystallin. It normally existed as aggregated structure consisting of 20~40 subunits. The determinations of oligomeric structure of  $\alpha$ -crystallin were also tackled with various state-of-the art experimental techniques due to the unavailability of its crystal structure, however no consensus on the oligomeric structure such as average number of subunits, degree of heterogeneity, spatial configuration of each subunit has been obtained. In addition, the experimental proofs for cooperative subunit kinetics between  $\alpha$ -crystallins have been reported by fluorescence resonance energy transfer (FRET), isoelectric focusing method and mass spectrometry. Hence,  $\alpha$ -crystallin are continuously engaged in cooperative subunit kinetics between  $\alpha$ -crystallins and they can exist as “*Dynamic quaternary structure*” mediated by such subunit kinetics. We therefore can only access to their inherent feature through disclosing the mechanism of cooperative subunits kinetics in  $\alpha$ -crystallin.

One of the most fascinating properties in neutron scattering is its ability for discerning hydrogen (H) and deuterium (D) through the difference in neutron scattering lengths between them. Deuteration assisted small-angle neutron scattering (DA-SANS) must be a promising method for tracking subunit kinetics in  $\alpha$ -crystallins. In addition, mass spectrometry is an unique experimental method for taking the snapshot of distribution of aggregation number.

In this presentation, we studied subunit kinetics of homo-aggregate of  $\alpha$ B-crystallin through the complementary use of DA-SANS and mass spectrometry.



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- Soft matter
- Small angle scattering

# The correlation between the mechanics of a lipid membrane and its cellular functions

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The spontaneous curvature,  $C_0$ , and the bending modulus,  $K_{cp}$ , are two collective properties of a lipid membrane. These two properties manifest the mechanics of a biomembrane and are intertwined with its biological functions. Contrary to the common perception, biomembranes assume nonlamellar structures in many cellular events, with the tendency of forming a nonlamellar structure quantified by  $C_0$  and with the extent of the ease to deform biomembranes measured by  $K_{cp}$ . In this presentation, the physical principles associating the mechanics with the functions of biomembranes and the biological relevance of the two collective properties are revealed through exploring the correlations between  $C_0$  and  $[Ca^{2+}]$  ( $[Ca^{2+}]$  is an important factor in many cellular events that involve the formation of nonlamellar biomembranes), and through those between  $C_0/K_{cp}$  and the membrane fusion (membrane fusion is a collection of cellular events that see two disparate membranes, as well as the volumes enclosed by them, merged). From the  $C_0$ - $[Ca^{2+}]$  correlations of different lipid species, we recognize that the charge density of the lipid headgroup is dominant in dictating the structural preferences of anionic phospholipids, and that displaying differential  $C_0$  sensitivities to  $[Ca^{2+}]$  is crucial for anionic phospholipids to fulfil their differential biological roles. Furthermore, the dependence on the two collective properties of the fusion capability indicates that an inter-membrane interaction that has seldom been characterized is in fact important to the fusion efficiency of a lipid membrane, and that the negative  $C_0$ -induced promotion of fusion is enabled via increasing the energetic cost of maintaining the membranes in the planar conformation, with respect to transforming them to the nonlamellar structures of the fusion intermediates.

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- Soft Condensed Matter/Biological Liquid Crystals
- Applications of High Pressure Physics
- Application of Scattering and Crystallography Techniques

# Structural insights into molecular assembly in the proteasomal systems

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The proteasome is a huge proteolytic machine consisting of a number of subunits. For example, the catalytic core particle is composed of seven different homologous  $\alpha$ -subunits and seven different homologous  $\beta$ -subunits. Accumulating evidence has revealed that the assembly of the eukaryotic proteasome is not spontaneous self-organization but an ordered process assisted by assembly chaperones that transiently associate with the assembly intermediates. Although several proteasome assembly intermediates have been identified, a blueprint for molecular assembly of this huge machine remains to be clarified. We performed biophysical studies of human proteasome subunits  $\alpha 6$  and  $\alpha 7$  and revealed that the isolated  $\alpha 7$  subunit exclusively exists as homo-tetradecamer in solution. We also proposed a “scrap and build” mechanism whereby its double-ring structure is disassembled upon the addition of  $\alpha 6$ , resulting in a 1:7 hetero-octameric  $\alpha 6$ - $\alpha 7$  complex [1].

In this study, we performed comprehensive biophysical studies including analytical ultracentrifugation, mass spectrometry, X-ray crystallography, electron microscopy, and high-speed atomic force microscopy in the eukaryotic and archaeal proteasomal systems. In the eukaryotic system, we expand our previous investigations on human  $\alpha 6$ - $\alpha 7$  subunits to include the five remaining  $\alpha 1$ - $\alpha 5$  subunits to gain structural insights into  $\alpha$ -ring assembly mechanisms. In contrast to the eukaryotic proteasomes, archaeal proteasome subunits are spontaneously assembled. Nevertheless, recent bioinformatic analysis identified archaeal homologs of proteasome assembly chaperones. We demonstrated that these archaeal homologs adopt quite distinct quaternary structures, i.e., homo-tetramer, homo-pentamer, and hetero-eicosamer, as compared with the hetero-dimeric eukaryotic counterparts. We will present our latest results regarding dynamic processes of proteasomes and interactions of the related proteins.

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- Structural biology
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- X-ray crystallography

# **Current Status and Results on J-PARC/MLF**

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Last year, MLF has started operation from February 22 after the recovery from a small fire incident in the second experimental hall. It stopped again due to a leakage of cooling water from the neutron target vessel on April 30 during the 500 kW proton beam operation. After the improvement of the target vessel, MLF restarted on October 27 at 500 kW for the user program. However, it stopped again due to the cooling water leakage from the neutron target vessel. We are now investigating the cause of the problem to develop a new type target vessel. The user program will restart at low power (~200 kW) in the middle of February 2016 by replacing the neutron target vessel to a reserved one.

In MLF, 21 neutron instruments have been funded. Within these instruments, 19 are in operation for the user program and 2 instruments are under commissioning or construction. Now the experimental hall is almost full with instruments, leaving only 2 ports are available for instruments in future.

World-class scientific outputs have been already created in various scientific fields, ranging from basic science to industrial application. Since J-PARC is internationally open for users, we have got experimental proposals from abroad more than 10% of the whole proposals. More than 20% of proposals have come from industrial users and a half of them are proprietary use. This fact has revealed a new horizon has come in the neutron scattering science in the 21st century.



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- Small Angle Scattering
- Quasi-Elastic Neutron Scattering
- Tribology

# Nanostructured Networks in Chiral Block Copolymers

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The designs of nanostructured materials and corresponding morphologies have attracted intensive attention because of their effectiveness in tuning electronic, optical, magnetic, and catalytic properties as well as mechanical properties. Nanostructured networks are perhaps the most fascinating morphology due to their high porosities and large specific surface areas as well as superior mechanical properties with self-supporting character. Although many technologies have been explored to fabricate nanostructured networks, self-assembly is one of the most important approaches to fabricate nanostructured materials with precisely controlled structures and morphologies from constituted components. Here, we aim to exploit the self-assembly of degradable block copolymers with chiral segments as a powerful tool to fabricate well-defined nanostructured networks. Subsequently, the fabrication of well-ordered nanoporous polymers with continuous nanochannels from the self-assembly of degradable block copolymers (BCPs), such as gyroid-forming network morphologies, can be obtained by degeneration of constituted segment(s) and used as templates for syntheses of various materials with different entities.

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- Self-assembly of Macromolecules and Supramolecules
- Hybridization of organic and inorganic Materials
- Nanopatterning Technologies from Bottom-up Methods
- Block Copolymer Physics
- Crystallization Behavior of Polymers

# Hierarchical Structure of Polymer/Nanoparticle Hybrid

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Using small angle X-ray scattering (SAXS), we elucidated the spatial organization of palladium (Pd) nanoparticles (NPs) in the polymer matrix of poly(2-vinylpyridine) (P2VP) and the nature of inter-nanoparticle interactions, where the NPs were synthesized in the presence of P2VP by the reduction of palladium acetylacetonate ( $\text{Pd}(\text{acac})_2$ ). The experimental SAXS profiles were analysed on the basis of a hierarchical structure model considering the following two types of interparticle potential: (i) hard-core repulsion only (i.e., the hard-sphere interaction) and (ii) hard-core repulsion together with an attractive potential well (i.e., the sticky hard-sphere interaction). The corresponding theoretical scattering functions, which were used for analysing the experimental SAXS profiles, were obtained within the context of the Percus-Yevick closure and the Ornstein-Zernike equation in the fundamental liquid theory. The analyses revealed that existence of the attractive potential well is indispensable to account for the experimental SAXS profiles. Moreover, the morphology of the hybrids was found to be characterized by a hierarchical structure with three levels, where about six primary NPs with the diameter of ca. 1.8 nm (level one) formed local clusters (level two), and these clusters aggregated to build up a large-scale mass-fractal structure (level three) with the fractal dimension of ca. 2.3. The scattering function developed here is of general use for quantitatively characterizing the morphological structures of polymer/NP hybrids and in particular for exploring the interaction potential of the NPs on the basis of the fundamental liquid theory.



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- Self-organization of DNA complexes for gene delivery and biomimetics
- Phase behavior of block copolymers
- Molecular aggregation of conjugated polymers
- Hierarchical structure of polymer nanohybrids

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